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THE SYNTHESIS AND ORGANIC CHEMISTRY OF THE
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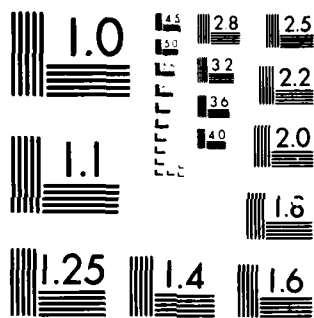
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THE SYNTHESIS AND ORGANIC CHEMISTRY OF THE BORON-SILICON BOND

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DECEMBER 12, 1985

U.S. ARMY RESEARCH OFFICE

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UNIVERSITY OF PUERTO RICO-RIO PIEDRAS CAMPUS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The synthesis of the boron-silicon bond via the reaction of methyldiphenylsilyllithium with 9-borabicyclo[3.3.1]nonane and treatment of the hydridoborate complex with acid was accomplished. The B-silyl-9-BBN was difficult to separate and purify, but was nevertheless fully characterized. It showed very little reactivity, however. For example, it oxidized well with		

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alkaline hydrogen peroxide and slowly in air, but was inert to methanol, water, bromine and tributyltin hydride. In addition it did not react with carbonyl compounds, nor with olefins or acetylenes under a variety of conditions. The reaction of silyllithium reagents with 9-BBN in the presence of N,N,N',N'-tetramethylethylenediamine produced the corresponding borate in excellent yield as judged by ^{11}B NMR analysis. These systems too were very unreactive, reacting well only with unhindered alcohols and very poorly with aldehydes and even acid chlorides. Attempts to prepare a stable, crystalline amine complex were unsuccessful.

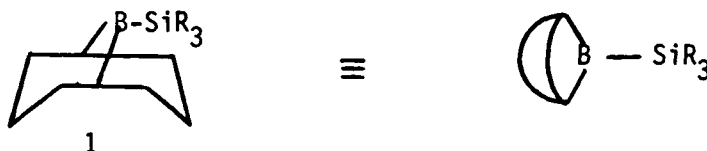
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Scientific Report

At the outset of this work we set out to prepare and study the structure, properties and chemistry of a trigonal organoboron which contained both the boron-silicon bond and carbon ligands (as opposed to oxygen or nitrogen ligands) on the boron. Our interest was to hopefully discover a new reaction, namely that of silaboration with this new class of compounds. Very little was published on this topic at the time we initiated our work and what was published indicated that the "ate" complexes of organoborons containing the boron-silicon bond were much more stable than the trigonal species that we were after.

One graduate student worked on the project the whole time and we concentrated our efforts on the 9-borabicyclo[3.3.1]nonane (9-BBN) systems **1** since it represented the most readily available starting materials and also the possibility of a rather stable product.

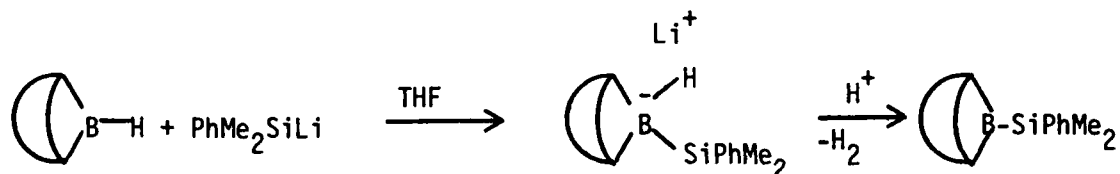


Treatment of B-methoxy-9-BBN with phenyldimethylsilyllithium in THF gave a product, which in the same solution showed several peaks in the ^{11}B NMR spectrum. On the other hand, treatment of 9-BBN with this same reagent gave different results depending on the source of the 9-BBN. A tetrahydrofuran solution of 9-BBN purchased from Aldrich reacted to give lithium dihydridoborato-BBN and the bis-silylated species as adjudged by ^{11}B NMR. This same reaction with freshly prepared and

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recrystallized 9-BBN gave a solution of B-(phenyldimethylsilyl)borato-9-BBN as evidenced by a doublet in the ^{11}B NMR spectrum at -18.94 ppm ($J = 80.6$ Hz). Treatment of this solution with hydrochloric acid or methane sulfonic acid in ether resulted in a high-boiling liquid, which was extremely difficult to purify. This material showed the following properties, which are consistent with the proposed structure 2: bp $112-113^\circ/0.12\text{mm}$ ^{11}B NMR 58.9 ppm; ^{13}C NMR $139.3, 134.3, 128.9, 128.2, 33.8, 23.7, -3.3$ ppm; ^1H NMR $7.75-6.75$ (m, 5 H), $2.0-0.35$ (m, 14 H), 0.20 (s, 3 H) ppm; MW by boiling point elevation in benzene 260 ; Anal. Calcd. for $\text{C}_{16}\text{H}_{25}\text{BSi}$: C, 74.98 , H, 9.76 , B, 4.29 , Si, 10.90 . Found: C, 74.85 , H, 9.96 , B, 4.02 , Si, 11.14 .



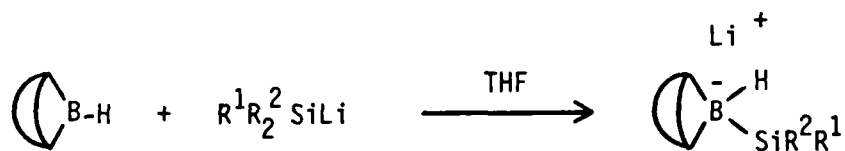
This material could be oxidized with alkaline hydrogen peroxide or in the air, although the air oxidation is somewhat slow. It reacted only slowly with acetic acid and not at all with methanol, water, bromine or tributyltin hydride.

Interestingly 2 did react with organolithium and organomagnesium reagents to give the B-alkyl-9-BBN derivatives although in poor yield.

All attempts to get 2 to react with carbonyl compounds or double or triple bonds failed.

We have recently found that 9-BBN reacts with silyllithium reagents in the presence of N,N,N',N'-tetramethylethylenediamine

to give cleanly the B-silyl-9-Borato-BBN derivative. Examples of this reaction are given in Table I. Attempts to carry out reductions with this material **3** gave disappointing results apparently due to the steric hinderance in the system. It does, however, react with certain alcohols to liberate hydrogen and produce the trigonal organoboron, which again has proved to be very difficult to purify. Results of this reaction are given in Table I.



- a) $\text{R}^1 = \text{R}^2 = \phi$
- b) $\text{R}^1 = \phi \text{ R}^2 = \text{Me}$
- c) $\text{R}^1 = \text{Me} \text{ R}^2 = \phi$

Table I:

Compound	Solvent	^{11}B NMR*	Solvent	^{11}B NMR*
$\text{LiPhMe}_2\text{Si-9BBN}$	THF/TMEDA	d 19.44 ppm	THF	t 17.57 ppm
		$J_{\text{B-H}} = 78 \text{ Hz}$		$J_{\text{B-H}} = 73\text{Hz}$
	THF/TMEDA			d = 19.70 ppm
				$J_{\text{B-H}} = 78 \text{ Hz}$
$\text{LiPh}_2\text{MeSi-9BBN}$	THF/TMEDA	d 19.83 ppm	THF	d 19.83 ppm
		$J_{\text{B-H}} = 78 \text{ Hz}$		$J_{\text{B-H}} = 78\text{Hz}$
$\text{LiPh}_3\text{Si-9BBN}$	THF/TMEDA	d 19.91 ppm	THF	---
		$J_{\text{B-H}} = 78 \text{ Hz}$		

*coupled spectra

Publications:

"The Preparation and chemistry of the Boron-Silicon Bond",
MSc thesis, University of Puerto Rico-Rio Piedras Campus,
March 1984.

Scientific personnel

Luis del Valle, graduate student.

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